

Research Article

MgO/ZrO₂ Promoted with SrO and CsO as a Reusable Nano Catalysts for One Pot Synthesis of 2-Amino-2-Chromene

Kiwaan HA*, Mohamed F, Elgindy HM and Mostafa MR

Department of Chemistry, Faculty of Science, Damietta University, Egypt

Abstract

MgO-ZrO₂ powder (MZ30) containing 30 wt% MgO was prepared by simple precipitation method. Two other catalysts were obtained by loading MZ30 powder with 5 wt% SrO and CsO using incipient wetness impregnation method. The catalytic performance of these catalysts was evaluated for synthesis of 2-amino-2-chromene via one pot three components condensation of benzaldhyde with malononitrile and α -naphthol. Different techniques such as N₂ physisorption, TGA-DTA, XRD, TEM, Hammet indicator method and CO₂-TPD have been used to characterize the investigated catalysts. Reaction paameters such as reaction temperature, synthesis time and catalyst amount were studied to optimize the reaction conditions. The observed activity of these catalysts were correlated to their basicity and other surface parameters. Synthesis of 2-amino-2-chromene may involve moderate and strong basic sites of PKBH+ in the range ≥ 9.8 and ≤ 15.0. Base sites of PKBH+ are too weak to contribute in the synthesis processes.

Keywords: MgO-ZrO₂ support; SrO; CsO additives; Chromene

Introduction

Synthesis of valuable compounds and pharmaceuticals can be carried out in the presence of both basic and acidic homogeneous or heterogeneous catalysts. Most of these processes were focused on the usage of homogeneous catalysts. It is well known that more than 1.6 million tons of fine chemicals were produced worldwide every year using homogeneous base catalysts such as NaOH and KOH, almost 30% of the selling price is for product separation, purification, recovery and waste treatment [1,2]. On contrary, heterogeneous catalysts have many advantages over their liquid counterparts such as they can be removed from reaction mixture by simple physical methods and can be reused several times after activation and cause fewer disposal problems, resulting in a more environmentally benign and economical process for the synthesis of fine chemicals. Therefore, the development of active and selective heterogeneous catalysts instead of conventional homogeneous ones has received much attention [3,4]. 2-Amino-2-Chromenes and their derivatives are of considerable interest as they widely employed as pigments, potential agrochemicals, and cosmetics and possess a wide range of biological properties such as anticancer, anticoagulant and antianaphylactic activity [5-7]. Currently the preparation of these compounds involves the three-component condensation of aldehydes, activated methylene compounds and activated phenols in organic solvents (i.e., acetonitrile, ethanol) using basic liquid catalysts such as piperidine [8]. In the past decade a considerable variety of relatively benign solid base catalysts such as basic Al₂O₂ [9] KF treated alumina [10], Ionic basic liquids [11] and MgO [12] have been studied for the synthesis of 2-amino-2-chromene. However most of these investigations are limited due to longer reaction time, moderate yields of the products and laborious workup procedure.

In the same context mixed oxides containing MgO catalysts are widely used as solid base catalysts in many catalytic processes such as aldol condensation [13-15], transesterification of triglycerides and biodiesel production [16,17]. However, to the best of our knowledge no study was devoted to the use of MgO-ZrO₂ system as a catalyst for synthesis of 2-amino-2-chromene. The effects of thermal treatment and the doping with SrO and CsO on surface characteristics were also studied. The catalytic activity of these catalysts towards the synthesis of 2-amino-2-chromene was evaluated. The synthesis conditions such as catalyst amount, reaction temperature and reaction time as a function of% chromene yield was also investigated.

Experimental

Catalysts preparation

MZ30 gel with 30 wt% MgO loading was obtained via coprecipitation method by dissolving the required amount of magnesium chloride and zirconium tetrachloride in 500 ml of deionised water. The mixture was mixed homogeneously and allowed to precipitate using basic solution of 1M KOH. The addition of KOH was continued at room temperature with vigorous stirring until pH~10. The gel formed washed several times with deionized water till free from chloride ions, then drying at 110°C for 12 hrs. Four thermal products were obtained by calcination of MZ30 sample at 723, 823, 923 and 1023 K respectively. The four calcined samples herewith referred as MZ30I, MZ30II, MZ30III and MZ30IV respectively. For subject of comparison pure ZrO₂ sample (Z) was also prepared and calcined with the same method. Two other samples doped with 5 wt% SrO or CsO were prepared by incipient wettness impregnation method. The obtained MZ30 gel was impregnated with aqueous solution of Sr(NO₃), or Cs(NO₃), containing the required amount of SrO or CsO. The obtained pastes were dried at 110°C for 12 hrs, followed by calcination at 923K for 6 hrs. The two samples named as SMZ30III and CMZ30III respectively.

Catalyst characterization

Shimadzo DTA-50 thermo-analyzer was used to evaluate the thermal behavior of various uncalcined samples, while X-ray diffraction (XRD) patterns of the samples were recorded on PAN Alylical, Xpert

*Corresponding author: Kiwaan HA, Department of Chemistry, Faculty of Science, Damietta University, Egypt, Tel: 2403866057; E-mail: hkiwaan@gmail.com

Received December 18, 2017; Accepted December 21, 2017; Published December 30, 2017

Citation: Kiwaan HA, Mohamed F, Elgindy HM, Mostafa MR (2017) MgO/ZrO₂ Promoted with SrO and CsO as a Reusable Nano Catalysts for One Pot Synthesis of 2-Amino-2-Chromene. J Chem Eng Process Technol 8: 368. doi: 10.4172/2157-7048.1000368

Copyright: © 2017 Kiwaan HA, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

J Chem Eng Process Technol, an open access journal ISSN: 2157-7048

PRO diffractometer with nickel filtered Cu K α radiation (1.5405°A). Identification of the crystalline phases was made with the help of JCPDS files. Surface area and pore size analysis were determined from N₂ adsorption at 77°K using Quantachrome, Nova "model 3200".

Surface morphology of the catalysts was observed by the help of a transmission electron microscopy [JEOL] while the product was characterized from its FTIR spectra by using a Jasco infrared spectrometer (model 410). The basic properties of the investigated samples were probed by CO₂-TPD measurements. Prior to CO₂ adsorption 0.15 g of the sample was loaded in a quartz reactor between two quartz plugs and out-gassed for about 1 h at 180°C under a vacuum to eliminate surface contamination and then cooled down to room temperature in dry N₂ for 1 h. Subsequently the samples were exposed to CO₂ (10%CO₂/N₂) for 50 min followed by purging with dry N₂ for 30 min. TPD of the sample was estimated in a N₂ gas at a flow of 25 ml/ min. with heating rate of 10°C /min from 25 to 800°C. The desorbed CO₂ was converted to methane using hydrogen gas over a methanation catalyst (Ni/KieSelghur) at 673K which was monitored using flame ionization detector. For comparison, the base strength of the calcined samples was also examined using Hammett indicators method. The Hammett indicators used here were bromothymol blue (PkBH+=7.2), phenolphthalein (PKBH+=9.8), nile blue chloride (PKBH+=10.1) and 2,4-dinitroaniline (Pk BH+=15). To measure the amount of basicity, the catalyst was mixed with a known concentration of HCl and the remaining concentration of HCl was measured by titration with NaOH and finally the amount of HCl equivalent to the catalyst basicity was obtained [18].

Catalytic synthesis of 2-amino-2-chromene

In a typical exeperiment, a stoichiometric mixture of benzaldehyde (5 m mole), malononitrile (5 m mole), α -naphthol (5 m mole) and the desired amount of the catalyst was ball milled for 15 min. The resulting mixture was heated in a 50 ml round flask in a drying oven at the desired temperature. After completion of the reaction, 20 ml of methanol was added to the reaction mixture and refluxed for 10 min. The catalyst was removed by filteration and the excess of methanol was distilled off and the product was recrystallized from hot methanol and characterized from its melting point (209-210°C) and FTIR spectra.

The% yield of chromene was measured from the following equation:

Chromene yield(%) =
$$\frac{\text{weight of product}}{\text{theoretical weight}} \times 100$$

Results and Discussion

Catalyst characterization

Prior to calcination, the thermal behaviour of the prepared samples was monitored by TGA/DTA (Figure 1). Evidently all the samples showed a significant weight loss extended from room temperature to a round 400°C. This weight loss was accompanied by two successive endothermic peaks centered at ~75°C and 370°C respectively. The endothermic effect centered at ~75°C may reflect the loss of physisorbed water, while the peak centered at 370°C was attributed to the transformations of Mg(OH)₂ to MgO. An additional endothermic peaks at at 570°C and 615°C were also observed for CMZ30 and SMZ30 gels respectively, each endothermic effect was attributed to the decomposition of doping salt to its corresponding metal oxide, which was also found associated with weight loss stages as indicated from TGA diagrams (Figure 1). Moreover MZ30 gel showed an exothermic peak centered at 585°C which was related to the crystallization of amorphous zirconia to a tetragonal

metalstable phase [19]. The position of this endotherm is slightly shifted to higher temperatures for CMZ30 and SMZ30 samples suggesting that the interaction of CsO or SrO with amorphous phase of zirconia may retards the crystallization process.

Page 2 of 7

Figure 2 shows the XRD patterns of the MZ30 sample calcined at different temperatures. The XRD pattern of MZ30 sample calcined at 723K shows a broadened line at 20=30.3°C indicating thus a poorly crystalline structure. But at higher calcination temperatures \geq 823 K the XRD patterns of MZ30 samples show diffraction lines agree well with the tetragonal phase of crystalline ZrO, [JCPDS No.27-997]. The presence of periclase MgO phase was not detected for all MZ₂O calcined samples, indicating higher degree of incorporation of magnesium ions into the zirconia matrix. XRD pattern of pure zirconia sample obtained via similar procedure and calcined \geq 923 K consists of tetragonal phase as well as monoclinic phase. This clearly demonstrates that the addition of magnesia to zirconia may stabilize the tetragonal phase and inhibit the growth of ZrO₂ crystallites to a certain size compatible with the monoclinic phase. Figure 3 shows the effect of doping CsO or SrO on MZ30 gel and calcined at 923°K. The two samples exhibited XRD patterns almost similar to those observed in Figure 2 and only crystalline t-ZrO, phase was detected. No diffraction lines corresponding to strontium and cesium compounds were detected indicating good dispersion of strontium and cesium species in the MZ30 surface. It is also evident from Figure 3 that doping of MZ₃0 with 5 wt% CsO or SrO has no significant effect on the positions of t-ZrO₂ reflection lines indicating no distortion in the structure of MZ30 sample caused by the incorporation of the two cations although the relative intensity of these diffraction lines decreased. It seems that the deposition of large strontium and cesium cations on the MZ30 surface may attenuate the characteristic lines of t-ZrO₂ phase. Scherrer equation [20] was used to determine the crystallite size of the investigated samples using the diffraction line at 20=30.3 corresponding to t-ZrO, phase. Crystallite sizes are found to be in the range of 15.8 nm-30.4 nm for all catalysts (Table 1). It is important to remark that the crystallite size of MZ30 sample increases as the calcination temperature increased from 823K up to 1023K. After crystallization at 823K, the particles continue to increase in size with increasing thermal treatment through the process of sintering as supported by the increase of intensity and narrowing of the diffraction lines. Table 1 reveals also that doping of MZ30 sample with 5 wt% CsO or SrO and calcined at 923K slightly affected its structural characteristics. Thus the two doped samples measured slightly lower values of crystallite sizes and degree of crystallinity than undoped MZ30II sample.

TEM images of some selected samples and their corresponding SAED patterns are shown in Figure 4. It can be seen from Figure 4 that all the samples consisted of nanoparticles and cannot be distinguished between MgO and ZrO₂ particles. The SAED pattern of MZ30I showed that ZrO₂ in the sample existed in an amorphous structure in agreement with XRD data. The images indicated also that the nanoparticles of MZ30II and MZ30III catalyst are of a regular spherical morphology, attached to each other along their boundries and showed the spongelike mesoporous network and the particle size is typically in the range of 7-32 nm. Furthermore from SAED patterns, the existence of a well-crystallized tetragonal structure was also confirmed. The thermal treatment of MZ30 at 1023K (MZ30IV) resulted in an appreciable formation of agglomerates with relatively large particle size probably through the sintering process as complemented by XRD data.

The textural properties were measured from N_2 physisorption measurements. The isotherms obtained at 77 K for MZ30 sample thermally treated at different temperatures (Figure 5) correspond in all cases to type IV according to IUPAC classification with H_3 hysteresis loops [21], suggesting that the porosity of the samples are

J Chem Eng Process Technol, an open access journal ISSN: 2157-7048



Figure 1: TGA (Dash Line) and TDA (Solid Line) of a MZ30, B, CMZ30 and SMZ30 gels.



mainly composed of mesopores. Textural parameters of all samples are listed in Table 1. As indicated from this Table 1, incorporation of Ca. 30 wt% MgO into ZrO_2 lattice sample (blank support) decreased the surface area from 86 m²/g to 64.11 m²/g for the sample calcined at 923K. Table 1 reveals also that the surface area of MZ30 continuously decreases with increasing the calcination temperature from 723 K to

1023 K. This behaviour may be attributed to the sintering of ZrO₂ at higher calcination temperatures as indicated from the increase of the crystallite size of t-ZrO, as the calcination temperature increased. The total pore volume of MZ30 sample shows a decrease from 0.215 to 0.127 ml/g with rising the calcination temperature from 723 K to 1023 K. At the same time, the mean pore radius shows an increase from 23.3 A° to 89.3 A° as the calcination temperature increased. Table 1 indicates also that addition of 5 wt% of CsO or SrO to MZ30 sample slightly affected its surface characteristics. To differentiate between the types of the existing pores and to calculate the surface areas (m²/g), the method suggested by de Boer et al. [22] was also used. The VI-t plots revealed the predominance of the mesopore structure for all samples under investigation. Figure 6 shows the pore size distribution curves of some selected samples obtained from the analysis of the desorption branches of the isotherms based on BJH (Barrett-Joyner-Halenda) model. Evidently, relatively narrow pores lies in the mesopore range and located at 3-10 nm were observed for all samples.

Page 3 of 7

 $\rm CO_2$ -TPD profiles of pure $\rm ZrO_2$, MZ30, SMZ30 and CMZ30 samples calcined at 923 K are presented in Figure 7. Whereas the concentration of basic sites as obtained from acid titration method and strength distributions of these sites as estimated from Hammett indicator method are listed in Table 2. The strength of basic sites were classified according to their different carbon dioxide desorption temperature TD, to weak (TD <200°C), medium (200<TD<600°C) and strong (TD>600°C) [23]. Pure ZrO₂ calcined at 923 K (ZIII sample) showed only carbon dioxide desorption peak at 135°C related to the presence of bicarbonates (weak basic site) with PKBH+ \leq 7.2 (Figure 7). However incorporation of 30



J Chem Eng Process Technol, an open access journal ISSN: 2157-7048



Figure 4: TEM images of some selected samples.



Figure 5: N_2 -physisorption measurements of (a) MZ30I, (b) MZ30III and (c) MZ30IV samples.

wt% MgO to ZrO, induces an increase in the density of basic sites. The TPD profile shown in Figure 7 indicates that MZ30III contains three main CO₂ desorption peaks at 135°C, 275 and at 415. The peak located at 135°C is attributed to the interaction of CO₂ with weak base sites while those observed at 287 and 415°C can be attributed to the presence of bidentate carbonate (bridged and chelating) related to the presence of medium strength base sites, probably generated due to the presence of Mg_2^+ - O_2^- pair sites. The concentrations of these sites were found to increase as the calcination temperature increased (C.F column of Table 2). This trind may be due to the formation of defects due catalyst restructing at higher temperature [24]. However no variation in the base site strength was observed as a result of increasing thermal treatment. All samples measured base strength of pKBH+ \leq 9.8. Loading MZ30 gel with 5 wt% CsO or SrO and calcined at 923 K evidently improved its basic property. Several changes can be observed in the TPD profiles of the two samples (Figures 7). The peak corresponding to the weak basic sites presented in the TPD profile of MZ30III sample completely disappears. Furthermore, the incorporation of the two metal oxides onto MZ30 also leads to a substantial increase of medium strength basic sites in the following order CMZ30III>SMZ30III>MZ30III, similar to that of the total basicity. Finally an additional two peaks are observed in the TPD profiles of SMZ30II and CMZ30II samples in the region of strong basicity (TD>600°C). This might be due to the presence of monodentate carbonates (strong basic sites), probably correspond to isolated O^2 anions located in a particular position of the mixed oxides surface [24]. The base strength of the two samples fell in the range of 10.1 ≤ PHBH+ ≤ 15.

Catalytic synthesis of 2-amino-2-chromene

The effect of various reaction parameters such as reaction temperature (RT), catalyst amount (CA) and synthesis time (ST) on catalytic performance was studied to optimize the conditions for maximum chromene yield. MZ30III catalyst was chosen for this study and the results were illustrated in Figure 8 and 8a illustrates the chromene yield over MZ30III catalyst as a function of reaction temperature. The yield at ST of 60 min and CA of 150 mg was increased from 7% to 71% when the RT increased from 70°C to 100°C. Increasing RT to 110°C also provided high yield closer to that at 100°C. A further increase in RT beyond 110°C greatly lowered the chromene yield (42% at 130°C). The effect of CA on chromene yield was also measured (Figure 8b). The amount of MZ30III catalyst was varied from 50-250 mg for the reaction at 100°C. The yield obtained at ST of 60 min increased from 27% to 71.0% when the CA was increased from 50 mg to 150 mg. Using CA beyond 150 mg up to 250 mg resulted in similar chromene yield. It is well known that the ST is also an important factor affecting the yield of product obtained. Accordingly set of experiments with MZ30III catalyst was also carried out under synthesis time varying from 30 min to 120 min Figure 8c. It is evident from Figure 8c that the yield increases as the ST increased to a point at which the maximum yield (71%) was reached at 60 and 90 min. A further increase in the synthesis time to 120 min led to reduce the yield obtained. Thus from the above results it seems that RT of 100°C, CA 150 mg and ST 60 min. appear to be an appropriate reaction conditions for the synthesis of chromene with MZ30III catalyst.

The results obtained for the synthesis of chromene over the prepared catalysts at the optimized conditions are listed in column 5 of Table 2. Including also in this table the corresponding values of total basicity obtained from acid titration method and their basic strengthes. The data presented in Table 2 reveals the following:

(i) Pure zirconia calcined at 923 K was found inactive for catalyzing this reaction under our reaction conditions. This may be attributed to the presence of only weak basic sites on pure zirconia surface (Figure 7).



Citation: Kiwaan HA, Mohamed F, Elgindy HM, Mostafa MR (2017) MgO/ZrO₂ Promoted with SrO and CsO as a Reusable Nano Catalysts for One Pot Synthesis of 2-Amino-2-Chromene. J Chem Eng Process Technol 8: 368. doi: 10.4172/2157-7048.1000368

Page 5 of 7

(ii) The addition of 30% MgO to zirconia led to the formation of at least the required active sites for the reaction to proceed as indicated from the enhanced catalytic activity of MZ30III catalyst. The MZ30III catalyst possesses mainly moderate basic sites with low amount of weak basic sites. The moderate basic sites are generated due to the interaction between MgO and ZrO_2 . It seems that synthesis of chromene necessitates at least moderate basic sites of pKBH+ \geq 9.8 while the base sites of pKBH+ 7.2 are too weak to contribute in synthesis of chromene.

iii) Columns 2 and 5 of Table 2 reveal also that the extent of the surface was not an important parameter in the synthesis process. Moreover the synthesis ability increased with a decrease in the surface area.

(iv) The data including in Table 2 indicates also that SMZ30III and CMZ30III catalysts possess remarkably higher activities than MZ30III catalyst. This can be attributed to the presence of moderate base sites as

well as the presence of strong base sites generated on the catalyst surface as a result of loading MZ30III with 5 wt% SrO or CeO. Therefore, one can be concluded that medium and strong base sites with suitable amount of basicity are responsible for the high yield of chromene under the present investigation.

Reusability tests

The recovery and repetitive use of catalyst is an important characteristic from industrial view point. Reusability tests of catalysts calcined at 923 K were carried at optimum reaction conditions (RT=100°C, ST=60 min and CA=150 mg). Upon the completion of the first run the catalyst particles were recovered washed three times with 5 ml portions of methanol and dried at 115°C for 2 h and reused for the next run for chromene synthesis. The yield of chromene was determined after each run and the results are illustrated in Figure 8. As indicated from Figure 8 for all the three runs about 10% of % chromene yield





J Chem Eng Process Technol, an open access journal ISSN: 2157-7048

Citation: Kiwaan HA, Mohamed F, Elgindy HM, Mostafa MR (2017) MgO/ZrO₂ Promoted with SrO and CsO as a Reusable Nano Catalysts for One Pot Synthesis of 2-Amino-2-Chromene. J Chem Eng Process Technol 8: 368. doi: 10.4172/2157-7048.1000368

Page 6 of 7

Sample	Crystallitate size (nm)	SBET (m ² /g)	St (m²/g)	S _{micro} (m²/g)	S _{meso} (m²/g)	VP (ml/g)	r (A)
Ziii	15.8	86	83	-	83	0.204	28.6
MZ301	-	185	187	39.1	147.9	0.215	23.3
MZ3011	17.4	111.4	104	-	104	0.195	35.2
MZ30111	23.3	64.11	63.2	-	63.2	0.175	54.7
MZ301V	30.4	28.7	30.2	-	30.2	0.127	89.3
S/MZ30III	22	60	61	-	62	0.17	48
C/MZ30111	21.6	58	60	-	57	0.168	50

Table 1: Crystallite size and textural properties of tested samples.

Sample	SBET (m²/g)	Total (basicitY'a) (m.mole g)	Base strength (PKsH+)	Chromene yield (%) (b)
Ziii	86	0.2	7.2	O (No reaction)
MZ301	185	1.333	7.2-9.8	50
MZ3011	111.4	1.83	7.2-9.8	63
MZ30III	64.11	2.666	7.2-9.8	71
MZ301V	28.7	2.766	7.2-9.8	71
S/MZ30111	60	3.33	9.8-15	95
C/MZ30 III	58	3.36	9.8-15	97.8

a-As measured from acid titration method; b- Yield refers to the pure isolated product

Table 2: Basicity and % Chromene yield of catalysts calcined at 923 K.

was reduced at the end of the third run for each catalyst suggesting that the tested catalysts were catalytically stable. The reduction in the yield after each run may be due to the leaching of active species in the reaction medium [25]. However, no diffraction lines corresponding to the presence of SrO and CsO were detected by XRD indicating the good dispersion of the two cation species on MZ30 support. Among the three catalysts tested, C/MZ30III catalyst showed the best catalytic performance this catalyst possess the greater quantity and also variety of basic sites with base strength in the PKBH+ range of 9.8 and 15. The results indicated also that the synthesis of chromene necessitates at least base sites with moderate strength (pKBH+ \geq 9.8) and weak base sites with pKBH+ \geq 7.2 are too weak to contribute in synthesis of chromene.

Conclusion

MZ30III as a solid base catalyst and as a support was prepared by a simple copreciptation method while SMZ30III and CMZ30III catalysts were prepared by the wet impregnation method followed by calcination at 923K for 4 h. The prepared catalysts showed an excellent catalytic activity for synthesis of 2-amino-2-chromene. The characterization studies showed that Sr(NO₃)₂ and Cs(NO₃)₂ precursors were converted to SrO and CsO upon heating up to 923K, however no diffraction lines corresponding to the presence of SrO and CsO were detected by XRD indicating the good dispersion of the two cation species on MZ30 support. Among the three catalysts tested, C/MZ30III catalyst showed the best catalytic performance this catalyst possess the greater quantity and also variety of basic sites with base strength in the PKBH+ range of 9.8 and 15. The results indicated also that the synthesis of chromene necessitates at least base sites with moderate strength (pKBH+ \geq 9.8 and weak base sites with pKBH+ \geq 7.2 are too weak to contribute in synthesis of chromene.

References

- 1. Weisssermel K, Arpe HJ (1997) Industrial Organic Chemistry. 3rd edn. Wiley, p: 481.
- Mattiusi EM, Ponte HA (2015) Behavior analysis of a porous bed electrochemical reactor the treatment of petrochemical industry wastewater contaminated by hydrogen sulfide (H2S). Chemical Engineering Journal 275: 305-314.
- 3. Molinari V, Giordano C, Antonietti M, Esposito D (2014) Titanium Nitride-Nickel

Nanocomposite as Heterogeneous Catalyst for the Hydrogenolysis of Aryl Ethers. J Am Chem Soc 136: 1758-1761.

- Sun LB, Liu XQ, Zhou HC (2015) Design and fabrication of mesoporous heterogeneous basic catalysts. Chem Soc Rev 44: 50-92.
- Hafez EA, Elnagdi MH, Elagamey AA (1987) Nitriles in heterocyclic synthesis: Novel syntheses of benzo[b]pyrans, naphtho[1,2-b]pyrans, naphtho[2,1-b] pyrans, pyrano[3,2-h]quinolines and pyrano[3,2-c]quinolines. Chemical Communications 7: 1534-1538.
- Sofan MA, Taweel FME, Elnagdi MH, Liebigs L (1989) Studies on Cinnamonitriles: The Reaction of Cinnamonitriles with Cyclopentanone. Euro JOC, pp: 935-936.
- Varma RS, Dahiya R (1998) An Expeditious and Solvent-Free Synthesis of 2-Amino-Substituted Isoflav-3-enes Using Microwave Irradiation. J Org Chem 63: 8038-8041.
- 8. Elagamay AGA, Taweel FMAA (1990) Indian J Chem B 29: 885-889.
- Maggi R, Ballini R, Sartori G (2004) Zeolite HSZ-360 as a New Reusable Catalyst for the Direct Acetylation of Alcohols and Phenols under Solvent less Conditions. Tetrahedron Lett 39: 6049-6052.
- 10. Ballini R, Bigi FML, Conforti RH (2000) Catal Today 60: 305-309.
- Gong K, Wang HL, Fang D, Liu ZL (2008) Basic ionic liquid as catalyst for the rapid and green synthesis of substituted 2-amino-2-chromenes in aqueous media. Catalysis Communications 9: 650-653.
- Kumar D, Reddy VB, Misshra BG (2010) Recent contributions from the Baylis-Hillman reaction to organic chemistry. Tetrahedron 110: 5447-5674.
- Leon M, Faba L, Diaz E, Bennici S, Vega A (2014) Consequences of the ironaluminium exchange on the performance of hydrotalcite-derived mixed oxides for ethanol condensation. Appl Catal B Environ 102: 590-599.
- 14. Peng J, Li B, Chen N, Wang G, Luo F (2016) Nanotechnology in Catalysis. Catal Commun, p: 74.
- 15. Liang D, Li G, Liu Y, Wu J, Zhang X (2016) Catal Comm 81: 33-38.
- 16. Manriquez R, Gomez R, Hernandez JGC, Azuniga M (2013) Catal Today 21: 223-230.
- 17. Su YL, Wang H, Yan X, Pan D, Fan B, et al. (2016) Chem Phys Lett 663: 55-61.
- 18. Mguni LL, Mukenga M, Jalama K, Meijboom R (2013) Catal Commun 34: 52-57.
- 19. Li G, Li W, Zhang M, Tao K (2004) Catal Today 59: 593-595.
- 20. Cullity BD (1978) Ellements of X-ray Diffraction. Addison-Welsey.
- 21. Xu RR, Bang WQ (2004) Chemistry of molecular sieves and mesoporous materials. Science Press, Beijing, p: 17.

Citation: Kiwaan HA, Mohamed F, Elgindy HM, Mostafa MR (2017) MgO/ZrO₂ Promoted with SrO and CsO as a Reusable Nano Catalysts for One Pot Synthesis of 2-Amino-2-Chromene. J Chem Eng Process Technol 8: 368. doi: 10.4172/2157-7048.1000368

Page 7 of 7

- 22. de Boor JH (1958) The structure and properties of porous materials. New Journal of Glass and Ceramics.
- Dicosimo JI, Diez VK, Xu M, Iglesia E, Apestegufa CRJ (1998) Catal 17: 84-99.
 Tantirungrotechai J, Thepwatee S, Yoosuk B (2013) J Fuel 106: 279-284.
- 23. Armendia MA, Borau V, Jimenez C, Marinas A, Ma JM, et al. (2004) J Molecul Catal A: Chem 218: 81-90.